

# BURN-RATE MODELING AND COMBUSTION DIAGNOSTICS FOR ENVIRONMENTALLY FRIENDLY, SOLID ROCKET PROPELLANTS

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## ABSTRACT

Advanced, burn-rate, propellant modeling is critical for developing new rocket-missile and gun propellants for Future Combat Systems and for providing a fundamental screening tool that can result in substantial cost savings compared to missile and gun firings. In this paper, we report the detailed chemical kinetics and burn rate prediction of tri-amino-guanidinium azotetrazolate (TAGzT) and nitrocellulose (NC).

## 1. INTRODUCTION

Most composite formulations in tactical rocket and missile systems contain about 70 to 80% ammonium perchlorate (AP), an environmentally, hazardous compound. AP contributes to ground water pollution, and its combustion yields copious quantities of toxic hydrochloric acid and an undesirable smoke signature. Thus, it is desirable to replace it with insensitive, high-energy materials that are safer and have reduced smoke signatures.

We are employing advanced flame diagnostics and burn-rate, propellant modeling to characterize new oxidizers and high-energetic binders and nitrate esters with high-nitrogen compound additives, such as 5-aminotetrazole (5-AT), bis-tetrazolyl-amino-tetrazine (BTATz), or tri-amino-guanidinium azotetrazolate (TAGzT), to determine their viability in rocket-missile propellants for energy-managed systems that require lower sensitivity, greater range, and flexibility (Sausa and Anderson, 2005). In this paper, we report our modeling and experimental efforts on nitrocellulose (NC) and TAGzT.

## 2. EXPERIMENTAL APPARATUS AND MODELING

The experimental apparatus and modeling are described in detail in our previous publications (Anderson and Fontijn, 2005, Miller and Anderson, 2004, Sausa, Venizelos, and



**Figure 1. A photograph of our experimental apparatus. Apparatus consists of a low pressure burner equipped for MB-MS, LIF, and thin-wire thermometry.**

Cabalo, 2006, Venizelos and Sausa, 1998, and Venizelos and Sausa, 2000). Briefly, the burn rates of NC and TAGzT are calculated over a broad pressure range using Cyclops, a burn-rate predictor developed at the US Army Research Laboratory (Miller and Anderson, 2004). The predictor employs a detailed chemical mechanism containing about 400 elementary reactions involving 100 species, which we obtained from a critical literature review. We tested parts of this mechanism with our burner flame apparatus shown in figure 1 using  $\text{H}_2/\text{NH}_3/\text{N}_2\text{O}/\text{NO}_2/\text{Ar}$  flames. We measured the flame temperatures by thin-wire thermometry, and the stable and radical species concentrations by laser spectroscopy, molecular beam mass spectrometry, or both. The experimental species concentrations are then compared to those obtained with the SANDIA PREMIX flame code containing subsets of the detailed chemical mechanism.

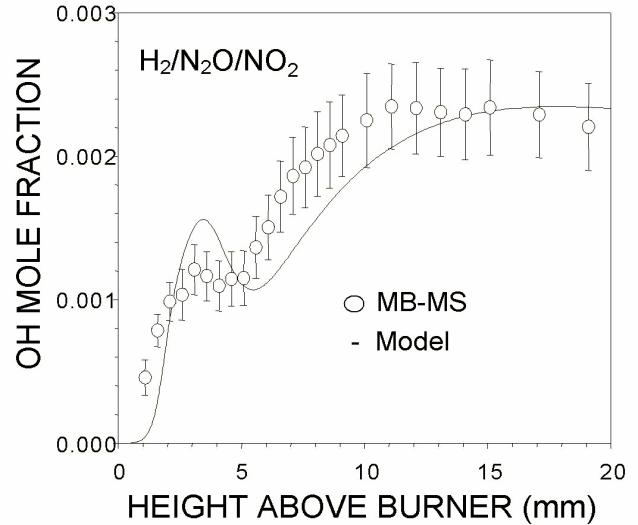
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### 3. RESULTS

The PREMIX calculations predict very well the  $\text{H}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{NO}_2$ ,  $\text{N}_2$ , and  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  stable species concentrations, as well as the  $\text{OH}$ ,  $\text{NH}$ , and  $\text{O}$  radical profiles in the flames studied. Figure 2 shows the experimental and modeled  $\text{OH}$  profiles for the  $\text{H}_2/\text{N}_2\text{O}/\text{NO}_2$  flame. The experimental LIF concentrations are converted to mole fractions using the measured flame temperatures and then normalized to the calculated mole fractions for comparison purposes. The model calculations predict well the shape of the  $\text{OH}$  radical throughout the flame, including a peak near 3.0 mm. Williams and Fleming observed a similar peak in their  $\text{OH}$  profile of premixed methane flames with  $\text{O}_2$  and  $\text{NO}_2$  oxidizers, and attributed it to the exothermic reaction  $\text{H}+\text{NO}_2=\text{OH}+\text{NO}$  (Williams and Fleming, 1991). Our model calculations also predict well the shapes of the  $\text{OH}$  profiles of the  $\text{H}_2/\text{N}_2\text{O}$  and  $\text{H}_2/\text{NH}_3/\text{N}_2\text{O}$  flames. The calculations show approximately a 55% decrease in the postflame  $\text{OH}$  mole fraction when ~4%  $\text{NH}_3$  is added to the  $\text{H}_2/\text{N}_2\text{O}$  flame. This decrease agrees well with the observed  $\text{OH}$  decrease of ~45% (Sausa, Venizelos, and Cabalo, 2006).

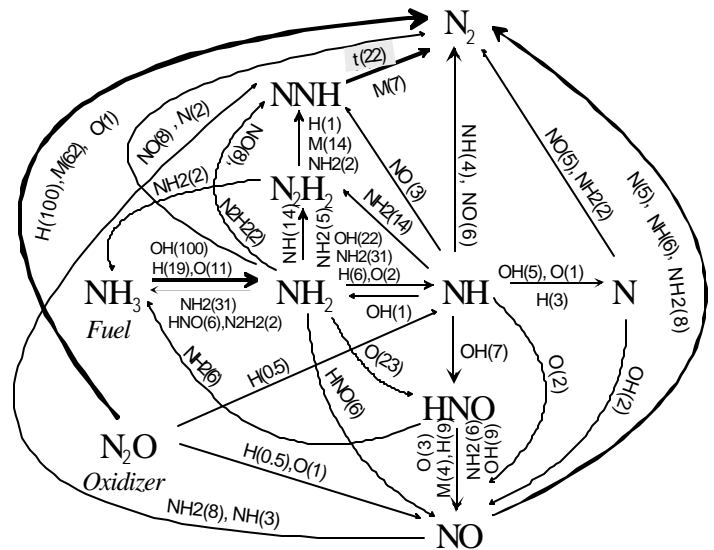
$\text{OH}$  rate analysis for the  $\text{H}_2/\text{N}_2\text{O}/\text{NO}_2$  flame reveals that  $\text{OH}$  is formed mainly from the reactions  $\text{NO}_2+\text{H}=\text{NO}+\text{OH}$  and  $\text{N}_2\text{O}+\text{H}=\text{OH}+\text{N}_2$ , and that it is consumed mostly from reactions  $\text{OH}+\text{OH}=\text{H}_2\text{O}+\text{O}$  and  $\text{H}_2+\text{OH}=\text{H}_2\text{O}+\text{H}$ . The peak observed in the  $\text{OH}$  profiles shown in figure 2 results from the interplay between reactions  $\text{NO}_2+\text{H}=\text{NO}+\text{OH}$  and  $\text{H}_2+\text{OH}=\text{H}_2\text{O}+\text{H}$ . In contrast, our  $\text{OH}$  rate analysis of the  $\text{H}_2/\text{N}_2\text{O}$  flame reveals that over 90% of  $\text{OH}$  is formed from the  $\text{N}_2\text{O}+\text{H}=\text{OH}+\text{N}_2$  reaction, and ~94% is consumed from the  $\text{H}_2+\text{OH}=\text{H}_2\text{O}+\text{H}$  reaction. A similar trend is observed for the  $\text{H}_2/\text{NH}_3/\text{N}_2\text{O}$  flame. However, the  $\text{NH}_3+\text{OH}=\text{NH}_2+\text{H}_2\text{O}$  reaction in the  $\text{NH}_3$ -doped flame plays more of a role in the consumption of  $\text{OH}$ , ~8%, compared to that in the neat flame (<0.01%).

Figure 3 is a pathway diagram of our modeled results showing the nitrogen chemistry occurring in the  $\text{NH}_3/\text{N}_2\text{O}/\text{Ar}$  flame. The numbers in parentheses are the relative integrated net reaction rates from 0 to 30.0 mm for the disappearance of the indicated reactant by the various reactions. These integrated rates are normalized to 100 ( $2.55 \times 10^{-5} \text{ mol/cm}^2\text{-sec}$ ) for the  $\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$  reaction. The  $\text{N}_2\text{O}$  reactant is consumed primarily by reactions



**Figure 2. Experimental and calculated  $\text{OH}$  profiles of  $\text{H}_2/\text{N}_2\text{O}/\text{NO}_2$  flame**

with  $\text{H}$  and  $\text{M}$  to form  $\text{N}_2$ , whereas its companion reactant,  $\text{NH}_3$ , is consumed by reactions involving the  $\text{OH}$ ,  $\text{H}$ , and  $\text{O}$  species to form  $\text{NH}_2$ .  $\text{NH}_3$  is regenerated to some extent mainly from  $\text{NH}_2$  species reacting with themselves. Although the reactions involving  $\text{N}_2\text{O}$  with  $\text{H}$  and  $\text{M}$  are the major routes for  $\text{N}_2$  formation, ~32% of  $\text{N}_2$  is formed from the  $\text{NNH}$ ,  $\text{NH}_2$ ,  $\text{NH}$ ,  $\text{NO}$ , and  $\text{N}$  species.



**Figure 3. Pathway diagram of an  $\text{NH}_3/\text{N}_2\text{O}$  flame**

Figure 4 shows a burning propellant and the nature of the burning propellant with thermochemical and physical processes that illustrate the complexity of the overall process. We modeled the gas phase at a high level of detail and finessed the condensed phase by a semi-empirical approach (Miller and Anderson, 2004).

Figure 5 shows both modeled and measured burn rates of nitrocellulose in the 1-100 MPa range, whereas figure 6 shows those of TAGzT in the 0.1 to 30 MPa range. Our model predicts the observed data extremely well for both NC (Miller and Anderson, 2004) and TAGzT (Tappen et al., 2006). We also computed the combustion products of TAGzT using our burn rate predictor at 1 MPa; their identity along with their mole fraction is as follows:  $N_2$  – 0.446;  $H_2$  – 0.211;  $NH_3$  – 0.120; and  $HCN$  – 0.220. These values agree well with those observed by Tappen and coworkers except for  $H_2$ , which they could not observe because of a limitation in their experimental apparatus (Tappen et al., 2006)

#### 4. CONCLUSION

Our advanced experimental and modeling capabilities provide the necessary tools for characterizing environmentally benign rocket-missile propellants with low sensitivity and signatures. We have developed a burning

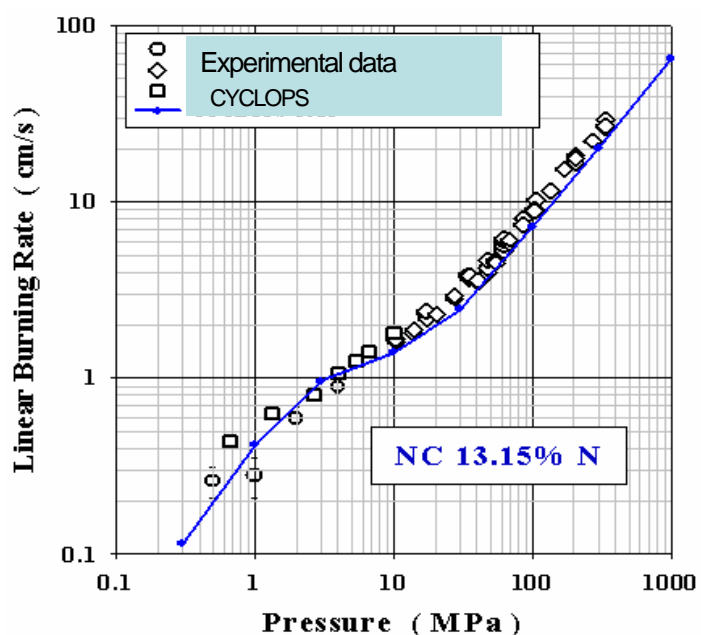


Figure 5. Calculated and observed burning rates of nitrocellulose

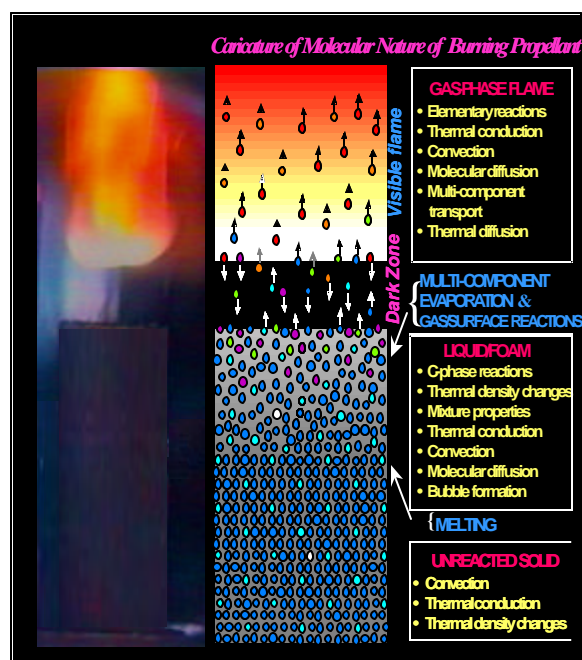


Figure 4. Molecular depiction (right) of a burning propellant strand (left).

rate model with detailed chemical kinetics for solid propellants, and presented our results for nitrocellulose and TAGzT. Overall, our model predicts very well the burn rates of NC and TAGzT over a wide range of pressure.

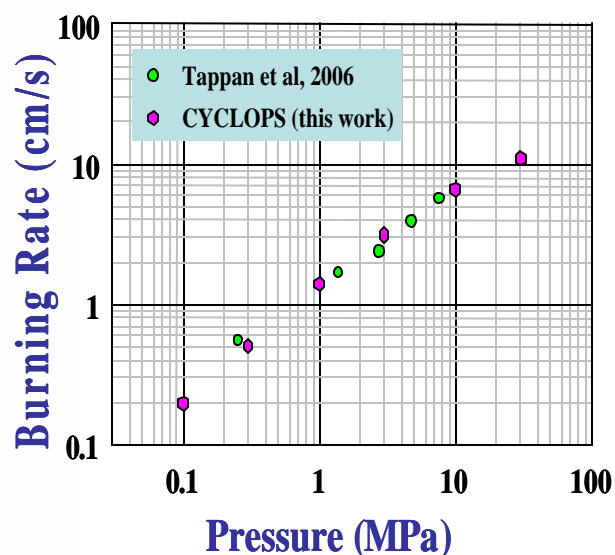


Figure 6. Calculated and observed burning rates of TAGzT.

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